THE SOURCES OF TITANIUM IN SILICEOUS SINTERS FROM CHILEAN HOT SPRINGS: IMPLICATIONS FOR MARTIAN SILICA. B. H. Trzcinski[1], M. Humayun[1], J. A. Gibbons[2], B. Zanda[3,4], F. Colas[3], A. Egal[3], L. Maquet[3], M. Reich[5], and C. Sanchez-Yañez[5], [1]Florida State University, Tallahassee, FL 32310, USA (bht14@my.fsu.edu; humayun@magnet.fsu.edu); [2]University of New Mexico, Albuquerque, NM 87131, USA; [3]IMCCE, Observatoire de Paris, CNRS UMR 8028, Paris F-75014, France; [4]IMPMC, Muséum National d'Histoire Naturelle, 75005 Paris, France ; [5]Universidad de Chile, Santiago, Chile.

Introduction: Hydrothermal settings are a potential habitat for living organisms on Mars. Silica deposits observed at Home Plate, Gusev Crater, Mars, have been argued to be formed in a hydrothermal setting based on their morphological similarity to terrestrial silica sinters from El Tatio, Chile [1]. If the silica at Home Plate is a hydrothermal sinter, then it is a potential astrobiological target for future Mars Sample Return.

Two hypotheses have been proposed for the origin of silica at Home Plate, (1): silica is a residue left behind after acid-sulfate leaching of metal cations from basaltic rocks [2]. (2): silica is a precipitate (sinter) from neutral-to-alkaline hot spring fluids [1]. The presence of opaline silica with digitate morphology similar in scale to terrestrial sinters from El Tatio geysers has added to the astrobiological potential of the Home Plate silica [1]. These digitate structures (microstromatolites) are considered to be of biological origin formed by silica-secreting microrganisms [1, 3]. The presence of substantial TiO_2 in Home Plate silica has been raised as potential evidence of residual origin [2], but anatase (a TiO_2 polymorph) is known from silica sinters and cherts on Earth [3-5]. Abundances of high field strength elements (HFSEs: Ti, Zr, Nb, Hf, and Ta) and other tracers help better understand Ti chemistry in terrestrial sinters. The objectives of this study are to ascertain whether the abundances of HFSEs (Ti, Nb, Ta, Zr, Hf) in sinters from terrestrial hot spring and geyser fields could be used to distinguish between an origin as an acid-sulfate residue or as a deposit from a hydrothermal setting. A second objective is to assess how effectively the hypotheses raised above for the origin of Martian silica could be assessed from returned Mars samples. For example, Ti is assumed to be immobile under acid leaching that would result in HFSE patterns of residual silica identical to that of the parent rock.

Analytical Methods: Active sinter samples were obtained from hot springs at El Tatio [6] and Puchuldiza [7], Chile, and paleosinters were also analyzed from Puchuldiza. The active sinters from El Tatio analyzed had the microstromatolite structure (Fig. 1) described by [1]. The samples were dissolved using HNO_3, HF and HCl. The resulting solutions were then chemically analyzed using a sector field inductively coupled plasma mass spectrometer (HR-ICP-MS), Thermo Element 2, at the NHMFL, FSU. Elemental abundances of 46 elements were determined. Procedural blanks and USGS basalt standards, BHVO-2, BCR-2 and BIR-1, were processsed together with the samples, and elemental abundances were obtained by reference against BHVO-2.

Fig. 1: Section of an active sinter sampled from El Tatio hot springs, U-1a, with fine laminations visible in section forming digitate structures on top (scale: about 2" across).

Results: TiO_2 abundances found in sinters from this study are shown in Fig. 2. All of the sinters from this study had TiO_2 abundances lower (<0.18 wt. %) than that reported from Martian silica [1], and from some terrestrial sinters from Iceland and New Zealand [8]. An *in situ* study of trace metals in Puchuldiza sinters found that most of the silica analyzed had <0.1 wt. % TiO_2, with only sporadic spots featuring higher abundances [7].

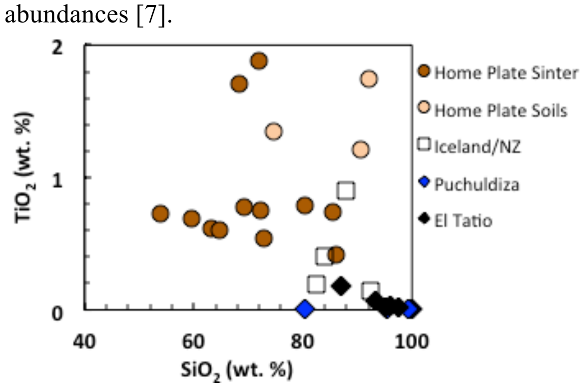

Fig. 2: SiO_2 vs. TiO_2 concentrations for sinters from El Tatio and Puchuldiza (this study) compared with silica deposits from Home Plate (Mars) [9], and sinters from Iceland and New Zealand [8].

The abundances of HFSEs are shown as CI-chondrite normalized patterns in Fig. 3. It can be seen that the sinters from Puchuldiza have the lowest HFSE abundances with a prominent deficit in Ti. The HFSE abundances in sinters from El Tatio are higher than those at Puchuldiza and have higher Nb/Zr and Ti/Zr ratios than the sinters at Puchuldiza. In Fig. 3, the measured sinter HFSE patterns are compared with patterns from basalts and with the composition of the Upper Continental Crust (UCC) [10] divided by 100 to place it at the same scale as the Puchuldiza sinters. The Puchuldiza sinters have a similar pattern to UCC, while the El Tatio sinters resemble BHVO-2 in their HFSE patterns.

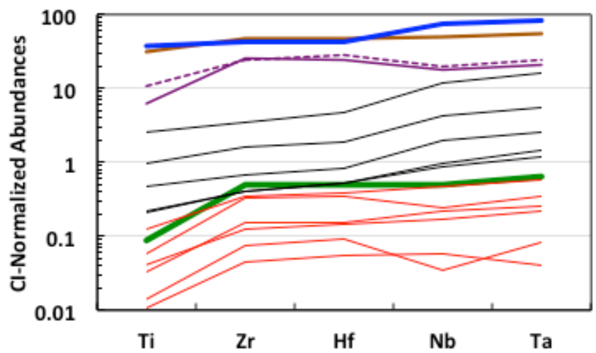

Fig. 3: CI-normalized abundances of HFSEs (Ti, Zr, Hf, Nb, Ta) in sinters from this study (red: Puchuldiza, black: El Tatio) compared with patterns for UCC/100 [10] (green), BHVO-2 (blue), BCR-2 (brown), and lavas from Nevados del Payachata/2 [11] (purple).

Rare earth element (REE) abundances correlated with the abundances of HFSEs in the sinters. REE patterns for both active and paleo sinters from Puchuldiza had a concave-upward pattern, with positive Eu anomalies and negative Ce (0.6-0.8) anomalies. In contrast, the REE patterns of El Tatio sinters had a sloping REE pattern steeper than that of BHVO-2 with no Eu or Ce anomalies.

Discussion: Anatase in terrestrial sinters has been considered to be residual, formed by acid-leaching of volcanic ash or of biotite that entered the hot springs [3-4]. Thus, the HFSE patterns of the El Tatio sinters are consistent with this interpretation if the volcanic ash had a pattern matching that of BHVO-2. The HFSE patterns of the Puchuldiza sinters are consistent with derivation from either felsic ash having a crustal HFSE pattern, like UCC, or from aeolian dust of UCC composition. No evidence is observed for significant fractionation of the HFSE patterns by solubility, even though any original Ti-bearing phases were likely recrystallized to anatase. The HFSE and REE patterns for the sinters at each location are controlled by local volcanic or Aeolian inputs into the hot spring basins. Source rocks through which the hydrothermal fluids percolate may play a role in the REE abundances, but are not likely to be significant for HFSEs, which are chemically more immobile. The closest active volcano to Puchuldiza, Isluga stratovolcano, is 27 km away. Numerous active volcanoes flank the El Tatio basin and are a likely source of immobile trace elements in the El Tatio sinters. The HFSE patterns of basalts from Nevado del Payachata (Chile) [11] are shown for comparison in Fig. 3. These basalts exhibit Nb-Ta depletion characteristic of subduction zone volcanism that is larger than that of the UCC.

Implications for Martian silica: The principal finding of this study is that HFSE patterns in silica sinters reflect the provenance of the material that falls into the hot springs, not its fluid composition. To discriminate the two hypotheses proposed for silica at Home Plate [1,2], we postulate that infalling tephra (e.g., Wishstone class) or the ubiquitous martian dust would be the dominant materials contributing HFSEs to siliceous sinters, while residues of acid-leaching would reflect local bedrock lithology. Since hydrothermal alteration tends to be localized, an HFSE pattern match to less altered versions of sampled bedrock would establish a residual origin for the silica. For effective HFSE finger-printing, a diversity of HFSE patterns in martian rocks and soils and a rover sampling strategy to optimize return of appropriate source material are required. Despite the powerful analytical capabilities of the Martian rovers, trace element data collected in this study is still possible only with ground-based laboratory techniques. This study has laid the groundwork for analyzing silica returned by future Mars missions, which would be a high priority due to the astrobiological potential of sinters.

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